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FATE AND TOXICITY OF THE HERBICIDE DICLOFOP-METHYL A LITERATURE REVIEW

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The Fate and Toxicity of the Herbicide Diclofop-methyl

I. Introduction

Diclofop-methyl ((+,-)-methyl 2-[4-(2,4-dichlorophenoxy) phenoxy]proprionate), otherwise known as HOE-23408, Hoelon, HOE-GRASS and Illoxan, is a phenoxyalkanoic herbicide introduced several years ago by Farbwerke Hoechst AG (Fig. 1, Table 1). It is extensively used in western Canada as a post emergence herbicide for control of wild oats and other grassy weeds such as yellow and green foxtail, barnyard grass, persian darnel and volunteer corn, in crops such as wheat, barley and flax. It is usually applied at the 2-4 leaf stage at rates of 0.84-1.40 kg/hectare (0.75-1.25 lb ai/acre) (Weed Handbook, 1983).

Both diclofop-methyl and its hydrolysis product diclofop acid (Fig. 2) have herbicidal activity. Top and root growth are arrested in susceptible plants, then wilting and chlorotic mottling occur on leaves. Utilization of carbon dioxide is drastically reduced (Weed Handbook, 1983). Diclofop-methyl inhibits several metabolic and auxin-dependant processes in plant cells (Hertel et al, 1983), such as chlorophyll synthesis and photosynthate translocation. It also inhibits calcium ion uptake into plant mitochondria and thus interferes with the regulation of the cytoplasmic Ca^{2+} activity. The ability of resistant species such as wheat to detoxify diclofop-methyl completely by aryl hydroxylation and subsequent conjugation is likely the basis for herbicidal selectivity (Shimabukuro et al, 1979, Jacobson et al, 1984). Herbicide placement in the plant and the rate of herbicide metabolism may also be factors in herbicidal selectivity (Shimabukuro et al, 1979).

Extensive use of wild oat herbicides on the prairies has led to concern over possible deleterious effects of these chemicals on man and his environment. In response to these concerns, recent research has focused on the toxicity of diclofop-methyl to wildlife which may be exposed to this herbicide in the natural environment. In addition, studies have investigated the effects of diclofop-methyl on species in the laboratory in an attempt to predict the harm to wildlife and man by chronic or acute exposure to this chemical.

The increase in the use of diclofop-methyl increases the exposure of man and wildlife. In order to predict the magnitude of this possibility for harmful exposure, an understanding of the fate and behavior of diclofop-methyl in the environment is necessary. Extensive research on the degradation, persistence and transport of this herbicide has been done in both terrestrial and aquatic environments, utilizing laboratory testing and commercial field use simulation tests. These investigations may lead to decreased hazard to man and his environment by the use of diclofop-methyl.

II. Fate of Diclofop-methyl in the Environment

1. Degradation in Terrestrial Environments

A considerable amount of research has been conducted on the behavior of diclofop-methyl in terrestrial environments. The degradation of this herbicide in soils has been studied extensively. Laboratory and field studies demonstrated that the formulated methyl ester applied to varying soil types undergoes an initial and rapid hydrolysis of the ester bond to the corresponding carboxylic acid ((+/-)-2-[4-(2,4-dichlorophenoxy) phenoxy]proprionic acid), followed by a much slower hydrolytic degradation(Smith et al, 1986, Martens, 1978, Gaynor, 1984, Smith, 1977, Wink et al, 1988, Smith, 1979a,b).

Subsequent degradation of the acid has also been characterized (Martens, 1978, Gaynor, 1984, Smith, 1977, 1979b). Martens (1978) applied ^{14}C-labelled diclofop-methyl to moist soils in flasks connected to aeration equipment to collect evolved $^{14}CO_2$ from the labelled herbicide for 25 weeks. Degradation products were identified by liquid scintillation counting and thin-layer chromatography. Further aerobic degradation products were detected, with a rapid dissipation of the hydrolysis product. The compound 4-(2,4-dichlorophenoxy) phenol (up to 10% of applied radioactivity) and trace amounts of six other unidentified metabolites were detected over time. Extensive degradation of the acid and its metabolites to a final product of evolved $^{14}CO_2$ occurred, accounting for 22-35% of the applied radioactivity. Martens suggested a possible degradation pathway for diclofop-methyl in soil by a cleavage of the ether bond between the aromatic and the aliphatic parts of the molecule. The ether bond could be cleaved either by direct hydrolysis to give lactic acid and the phenol, or by stepwise degradation of the side chain to ultimately give CO_2. Extensive mineralization of the aromatic rings was assumed, as indicated by liberation of $^{14}CO_2$.

Other studies examining the degradation of diclofop-methyl were also able to detect small amounts of the phenol metabolite of diclofop acid. In addition, small amounts of the metabolite 4-(2,4-dichlorophenoxy)phenetole were identified by thin layer chromatography along with traces of other nonidentified metabolites (Gaynor, 1984, Smith, 1977, 1979b). Smith (1977) (Fig. 3) postulated that the phenetole was formed from the acid by a decarboxylation process which is further dealkylated in the soil to the phenol. The direct conversion of the acid to the phenol was given as a possible mechanism. Smith also suggested that the phenol may undergo further degradation processes involving ring fission to give products such as n-dichlorobenzene or 2,4-dichlorophenol, and ultimately mineralization to carbon dioxide, which supports the degradation pathway suggested by Martens (1978).

A number of studies in both field and laboratory have indicated that combustion of radiolabelled diclofop-methyl treated soils demonstrates an increase in residues resistant to polar solvent extraction over time. Amounts of applied herbicide remaining in intimate contact with soil types as unextractable nonidentified residues at the end of the growing season were 33% (Gaynor, 1984), 38-52% (Smith, 1977) and 37% (Smith, 1979b) of applied radioactivity.

To determine the nature of the nonsoluble radioactivity associated with treated soils (Smith, 1977), samples were refluxed with hot aqueous triethanolamine. Thin layer chromatography led to the identification of the acid and phenol metabolites, so that it appeared that both of these degradation products could undergo a binding or complexing (either physical or chemical) to soils. Smith suggested that in soils some chemical reaction could occur involving the acid carboxylic grouping so that diclofop acid could become chemically linked to soil components.

Combustion experiments indicated that considerable amounts of bound residue were associated with the soil humic (Smith, 1977, 1979b) and fulvic fraction (Smith, 1979b). The identity of the bound radioactivity has not been fully established, but it has been suggested that incorporation of diclofop acid, as well as small fragments (resulting form fission of the herbicide ring system) into soil organic matter may contribute (Smith, 1979b). The phytotoxic significance of these bound residues are still unknown.

2. Persistence in Soils

Several studies indicate that diclofop-methyl is relatively nonpersistent in soil. Hydrolysis of the applied ester herbicide was nearly complete on all soil types (Smith et al, 1986,

Martens, 1978, Gaynor, 1984, Smith, 1977, 1979b, Wink et al, 1988, Wu et al, 1976) within a few days of application. Laboratory studies observed that extensive loss of the ester by degradation occurred in Regina heavy clay soil so that only 15% of the applied ester could be detected after 24 hours incubation of the soils (Smith, 1977). The half-life of the ester was determined in a separate experiment as <3 d (Wink et al, 1988). Under field conditions, diclofop methyl was also rapidly hydrolyzed as Saskatchewan field trials (Smith et al, 1986) agreed with Smith's findings in the laboratory. Degradation of the applied parent ester was complete and rapid in the field, so that after 9 d the ester could not be detected (Smith et al, 1986). Field plots in Ontario's moist, humid conditions (Gaynor, 1984) were similar to Smith's, so that diclofop-methyl recovery after 24 h was 20% and only 10% after 72 h.

Subsequent loss or degradation of the acid was much slower. In most studies, the acid could be detected as the major component throughout the growing season, along with trace amounts of its metabolites. Laboratory studies on varying soil types (Martens, 1978) demonstrated a 50% loss of diclofop acid within 6 to 38 d depending on soil type, with extensive liberation of CO_2 from mineralization of residues throughout the experiment, reaching a maximum at 30 d after application. Laboratory studies on soils by Smith (1977, 1979b) confirmed that the majority of extracted component was diclofop acid. After 70 d, the amount of the acid was 20% of applied herbicide. Less than 1% was present as the phenol and phenetole. Throughout the summer and fall during Saskatchewan field trials there was a slow reduction of the acid so that in October, 126 d after application, 19% of the original treatment was still detected. Treated field plots tested for persistence by Smith (1977) showed greater degradation, detecting only 5% of the applied herbicide at the end of the growing season and similarly, 8% of carry-over at the end of the season in a separate trial (Smith, 1979b). Field trials in Ontario (Gaynor, 1984) observed that the concentration of diclofop acid was reduced to 20-40% in 34 d. Less than 5% of the ^{14}C extracted after 34 d was identified as diclofop-methyl, phenol, or phenetole, suggesting that these metabolites do not build up in soil and are broken down as fast as they are formed. This confirms Smith's suggestion that these compounds do not accumulate in soil. The study showed similar results to Smith's field trials in that less that 14% of the applied radioactive labelled herbicide was detected at the end of the growing season (117 d) and no carry-over of phytotoxic residues to the next growing season was found.

As discussed earlier, the tendency of diclofop-methyl to degrade into metabolites which become bound to soils in increasing amounts with time raises concern over the possibility of persistent and potential phytotoxic residues in soil. Further

studies on this aspect have suggested that these bound residues do not pose a problem either with soil carry-over or phytotoxicity. Smith (1979a) treated small field plots over 2 growing seasons with diclofop-methyl at 1 kg/ha and extracted bound residues using aqueous triethanolamine. In both years, diclofop-methyl had undergone almost complete degradation with no significant amounts of ester or acid being detected (<2% ester, <7% acid). In addition, detectable amounts of bound residues were not found in either years, suggesting that bound residues derived from diclofop-methyl should be insignificant following normal field application.

The persistence of diclofop-methyl was studied using phytotoxicity as an indicator of the presence of active parent ester or metabolites in treated soil (Wu et al, 1976). Several species of grasses were used as indicators, including yellow foxtail, barnyard grass and Texas panicum in the greenhouse. Grain sorghum was used to bioassay for residual persistence in the field. Results of plant toxicity in the field showed no detectable soil phytotoxicity after 8 weeks post-treatment. This confirms Smith's findings (1979a) that, during normal field use of diclofop-methyl, bound residues do not persist to an extent great enough to be a problem. However, these results may also suggest that bound residues may be persistent but unavailable to plants or are transported to other areas. There was also no difference in persistence between soil-incorporated or surface-applied herbicide

3. Factors Influencing Fate of Diclofop-methyl

The persistence and degradation of herbicides in soil environments depend on a number of factors. Soil type (organic content, clay, silt, sand) and conditions of the soil such as pH, moisture content, and temperature, which may also influence microbial activity, can all affect the dissipation, transport and degradation of chemical in the soil.

a) Soil Characteristics

Several studies have examined the degradation rate and persistence of diclofop-methyl in differing soil types. The contents of sand, silt, clay and organic carbon which make up the soil will influence the fate of the herbicide. Soil characteristics which have been studied are summarized in Table 2.

Martens (1978) examined diclofop-methyl behavior in a loamy sand and a sandy soil. Results showed a slower loss of diclofop acid in the sandy loam. Behavior of diclofop acid in sandy soil showed a 50% loss in 6 to 9 d. Treated sandy loam showed a

four-fold slower degradation, with 50% loss occurring within 23 to 38 d. This suggests that properties of the experimental soil are deciding factors for dissipation of this herbicide.

Three soil types were compared for their effect on degradation rates in the laboratory (Smith, 1977). Sandy loam, silty clay and heavy clay were treated and examined for degradation products over time. Hydrolysis of the ester with subsequent degradation was most noticeable on the finer textured heavy clay and least on the silty clay. At the end of a 24 h period hydrolysis of the ester occurred at levels of 85% for heavy clay, 68% for loamy sand and only 40% for silty clay. At 70 d, only 20% of the initial ^{14}C was extracted from the sandy loam and heavy clay while 50% was recoverable from the silty clay, indicating poor hydrolysis of the parent ester in the latter soil type. Diclofop acid reached a maximum during the first week following ester treatment on the sandy loam and heavy clay, whereas a maximum was not reached till 7 to 21 d after treatment in the silty clay.

In a similar study, Smith (1979a) treated the same soils with diclofop-methyl and determined that the humic acid fraction of the soils was greatest in the Melfort silty clay and least in the heavy clay, and also found that diclofop acid recoveries were greatest from the heavy clay extracts and least from the silty clay extracts, suggesting adsorption of the acid to this fraction. Recoveries from heavy clay, loamy sand and silty clay using triethanolamine were 70%, 29% and 12% respectively, indicating that the acid was bound to a greater extent in the silty clay containing the largest proportion of humic acid.

The degradation of diclofop-methyl (Wink et al, 1988) was quicker in sand than in sandy loam. In addition, evidence for soil type influencing steriochemical inversion was presented. Steriochemical inversion was always greater for the S-enantiomer than the R-enantiomer, with 50% inversion in sandy loam observed in 4 d. Inversion was greater in sandy loam than in sand.

The evidence presented suggests that diclofop-methyl is degraded to a greater extent in soil types such as heavy clay and loamy sand where clay content is higher, resulting in a finer-textured soil. Several parameters of the soil in different experiments make it difficult to determine the specific characteristic of the soil which most influences degradation.

As Smith (1979a) suggested, the greater persistence of diclofop-methyl found in some soil types may be a result of various inherent properties of the soil, such as humic fraction. Other studies have suggested that the pH and moisture content (based on the intrinsic field capacity due to texture and organic content) of the soil type influence degradation rates, which may

partially explain the varying degradation rates in different soil types. Moisture content and pH affect degradation behavior both directly, and by indirect influence on microbial activity in soil and adsorption to soil fractions.

b) Influence of Soil pH on Degradation Rates

The adsorption of diclofop-methyl to humic fractions in soil may be influenced by pH (Smith, 1979a), therefore affecting the persistence of the herbicide. Smith suggested that in acidic soils, weakly acidic pesticides such as diclofop-methyl could be adsorbed to a greater extent that in a neutral form, thus making diclofop less available for microbial degradation.

The effect of soil pH on the fate of diclofop-methyl has been examined in laboratory studies (Gaynor, 1984). Gaynor showed that hydrolysis of the herbicide ester to its corresponding acid, diclofop, was slower at decreased pH on Fox sandy loam, with recoveries of diclofop-methyl after 24 h incubation being 40, 66 and 80% at pH 5.5, 6.5 and 7.5 respectively. After 72 h, 71% of the ester was hydrolyzed to the acid at pH 5.5, but 90% was hydrolyzed at pH 7.5, providing evidence that hydrolysis is affected by pH.

Soil pH had little effect on subsequent degradation of diclofop or metabolites formed, and persistence data for the three soil pH showed no significant difference on the last sampling dates. Studies (Martens, 1978, Smith, 1977, 1979a, Wink et al, 1988) suggested that the herbicide was more persistent in acid soils, however, these studies used different soil types for each pH level. Gaynor's results indicate soil pH had little affect on persistence. This is in contrast to other studies using differing soil pH and type, and may indicate that greater persistence may not solely be an effect of acidic pH, but rather that soil type, texture and organic matter have a greater influence on degradation of the herbicide than pH alone due to increased microbial activity and adsorption in certain soil types and textures.

c) Influence of Moisture Content on Fate

Research concerned with the influence of soil moisture on the degradation, persistence and phytotoxicity of diclofop-methyl has provided evidence that relative hydrolysis of the ester (Smith, 1977) and phytotoxicity (Mulder et al, 1979) of diclofop-methyl is greater in moist soils than in dry soils.

Application of diclofop-methyl on moist soils (85% field capacity), soils at 50% of field capacity and on air-dried soils (Smith, 1977) indicated that moisture has a strong influence on hydrolysis of the ester to its carboxylic acid. At 85% and 50%

field capacity the effect was small and hydrolysis in 24 h was 85% and 78% respectively. However on air dried soils, less than 5% of the ester treatments underwent conversion to the acid after 24 h.

Distribution and amount of rainfall during the growing season has been suggested to influence persistence of field-applied diclofop (Gaynor, 1984). Persistence of the herbicide in 1981 was greater than in 1980 in both sandy loam and clay soils. The 1980 study received rainfall shortly after application but in 1981 the rainfall pattern shifted to later in the season, which may have decreased the rate of degradation during that year. This may provide further evidence that moisture has a strong influence on the initial hydrolytic degradation of the parent ester to the acid soon after application, and less influence on later degradation to further metabolites. Decreased initial hydrolysis may allow the ester more time to adsorb to soil components, becoming less available to microbial degradation and increasing the persistence of the herbicide on initially dry soils.

Greenhouse studies examined the effect of moisture on persistence and degradation by examining the phytotoxicity and availability of Hoe 23408 (Mulder et al, 1979, Wu et al, 1976). Wild oat control was increased (Mulder et al, 1979) when soil moisture in Tiffany sandy loam increased from 18.5% to 23.5% (75% to 125% of field capacity), possibly due to increased absorption by the plant. Subsequent loss of moisture after application or watering delay did not have any significant interaction with diclofop concentration, further indicating the importance of moisture to initial degradation of the ester.

Wu et al (1976) showed degradation rates of diclofop-methyl, as measuered by phytotoxicity, could be affected by both temperature and soil moisture. At low moisture content (1.5% soil moisture), degradation rates were low and were similar at 4.4 C and 21 C. Similarly, high degradation rates were measured at 10% moisture at both 4.4 C and 21 C. At 5% soil moisture, however, degradation was significantly higher at 21 C than at 4.4 C. In this study, no detectable soil phytotoxicity remained after 8 weeks at 10% moisture at both temperatures or at 5% at 21 C. Phytotoxicity remained after 15 weeks at 1.5% moisture at both temperatures and at 5% soil moisture at 4.4 C.

The influence of soil moisture and temperature on degradation and persistence of diclofop-methyl may be partly correlated with the amount of microbial activity present in the soil. Microbial degradation of Hoe Grass was examined by determining degradation rates under aerobic and anaerobic soil incubation conditions (Martens, 1978). Activity recovered from radiolabelled treated soils under aerobic conditions indicated a

high capacity for degrading the herbicide in the presence of oxygen. In contrast, anaerobic conditions pointed to a small degree of degradation in the soil. In both cases, rapid hydrolysis of the ester occurred. However, under anaerobic conditions, further degradation of the acid was very limited. The only metabolite detected was small amounts of phenol. The phenetole and five other unknown metabolites identified in the aerobically incubated soils were not found in anaerobic soils. In addition, the extensive mineralization to CO_2 in the presence of O_2 did not occur in the anaerobic conditions for the full 25 weeks of the experiment.

In anaerobic experiments, the hydrolysis product was found to be very persistent, verifying poor degradation without the presence of oxygen. Aerobically, 50% of diclofop was lost within 6 to 38 d. However, under anaerobic conditions the loss is much slower; from the experimental data it was calculated that 150 d or longer was necessary for a 50% dissipation.

Comparison of the analysis of the effect of moisture content, pH and oxygen on degradation of diclofop-methyl suggest that each factor has influence on specific steps of the breakdown of the ester. Anaerobic experiments indicated little influence of microbial activity on the initial hydrolysis of the ester to the acid. However, both moisture and pH of the soil greatly influenced the degree and rate of ester hydrolysis. Similarly, subsequent degradation of the acid was influenced differently by these factors, with decreased microbial activity influencing persistence greatest. Moisture and pH decreases gave an increase in persistence of diclofop-methyl. However, it is difficult to separate direct influence from the affect of microbial degradation of the herbicide.

III. Fate of Diclofop-methyl in the Aquatic Environment

Very little research has been done on the degradation or persistence of diclofop-methyl in aquatic systems. Available work has provided evidence that persistence of the herbicide is limited. Research of the degradation pathways has not been done and partitioning of diclofop-methyl in water, sediment and aquatic organisms has been only partially examined (Knauf et al, 1977).

Studies of diclofop-methyl indicate a rapid dissipation. A shake-flask screening test (Walker, 1984) examined half-lives of the herbicide in natural waters and waters amended with underlying sediment. Half-lives for diclofop-methyl ranged from 0.17 d to 0.63 d in water and 0.04 d to 0.33 d in the water/sediment test. Also, the first order rate constants ranged

from 0.04565 to 0.19417 hrs^{-1} for water and 0.08832 to 0.53347 hrs^{-1} for water/sediment.

The shorter half-lives in the water/sediment system, which would include a biological component, demonstrate the influence of biological/microbial degradation. In addition, sterilization of both water and water sediment systems greatly increased persistence; half-lives were less than 50% of that in the active systems, indicating involvement of the sediment/water microflora in the degradation process. Half-lives ranged from 3.7 to 12.4 d in sterile water and 1.8 to 2.1 d in sterile sediment.

Natural ponds (Knauf et al, 1977) treated with 6.5 kg/ha rate diclofop-methyl verified the rapid degradation rates indicated in the screening test. Rapid hydrolysis to the acid occurred, which reached a maximum concetration in 24 h and declined thereafter to 30 d. Mud residue analysis detected the parent ester; however, the acid was not present, indicating adsorption of the neutral species.

Partitioning of diclofop-methyl in aquatic species was examined in the same study. Samples of algae, fish (Idus melamnotus) and snails (Planorbis corneus and Limnaea stagmalis) were analyzed for residue concentrations throughout the 30 d test period. Algal residues reached a maximum in 5 to 10 d and slowly declined thereafter. In fish and snails, residues reached a maximum in 1 to 5 d and then also declined.

Carp (Cyprinus carpio) was tested (Knauf et al, 1977) in the laboratory. They were exposed to three continuous dosages in a dynamic test system and residue measurements were taken after 4 weeks (1.0, 0.5 and 0.25 ppm treatments). Results were compared to concentrations in the surrounding water and an enrichment factor of 120-200 was calculated.

IV. Transport in the Environment

Movement of herbicides in the environment to nontarget areas can occur through several routes. Spray drift during application and post application losses such as movement in waters through leaching, surface runoff or by direct escape of the herbicide vapor to the atmosphere may all occur to varying degrees, dependent on the nature of the herbicide and environmental conditions. The transport of diclofop-methyl in the environment has been partially characterized.

Application losses, or drift, of diclofop-methyl has been investigated in field experiments (Smith et al, 1986). Diclofop-methyl was applied post-emergence in the field using a tractor-mounted sprayer at rates of 100 L/ha during wind speeds

of 4.41 +/- 0.35 ms^{-1}. Horizontal mass flow during spraying was monitored using air samples collected at three heights (50, 100 and 200 cm) on all four sides of the field. The drift of applied diclofop-methyl under these conditions was found to be minimal. The downwind diclofop-methyl ester mass drifting during the 2 h application period was calculated to be <0.1% of the amount applied. The low drift losses were considered to result from optimal operational and meteorological conditions during application.

1. Leaching Ability

Studies of post application losses of diclofop-methyl by leaching through soil (Mulder et al, 1979, Wu et al, 1976) show that soil mobility of the herbicide was negligible. Soil thick-layer chromatography was used for soil movement experiments (Wu et al, 1976) by monitoring symptoms shown by bioassay plants. Results showed that diclofop-methyl has the same degree of soil mobility as trifluralin, with R_f values in sandy loam of 0.02 and 0.04 in Cobb sand. Bioassays of soil samples from field trials indicated that all of the applied Hoe 23408 remained in the top 7.6 cm core.

The influence of soil type and moisture content on the leachability of ^{14}C-diclofop in soil columns of loam, a Wisconsin soil and four North Dakota soils (Table 2) was determined (Mulder et al, 1979). Soil columns treated with radiolabelled diclofop-methyl (equivalent to 1 kg/ha) were leached with 25, 50 and 100 mm water. Analysis of core samples of the soil columns indicated that the greatest leaching occurred in the coarser textured soils with 60% recovery in Fordville loamy sand compared to 34% in Fargo clay in the top 2 cm of soil columns. Movement indicated a strong correlation to clay content. However, similar to (Wu et al, 1976), more than 82% of the applied herbicide was recovered from the top 8 cm.

Studies on the effect of moisture on movement indicated that the eluted herbicide increased almost twofold when applied water increased from 25 to 100 mm.

The leachability of various herbicides has been related directly to water solubility and inversely to organic matter and/or clay content of the soil (Mulder et al, 1979, Hassan et al, 1987). A review on the transport of wild oat herbicides (Grover, 1984) attributed movement of herbicides to their intrinsic solubility, adsorption/desorption estimates for soil types and amount, timing and frequency of precipitation. Diclofop-methyl was cassified as a herbicide exhibiting little or no leaching potential due to low solubility and strong adsorption by weak physical forces.

2. Volatility

Potential evaporation or volatilization of herbicides is a function of their vapor pressure and environmental conditons. Diclofop has been classified as a herbicide with low or intermediate vapor pressure (3.0×10^{-8} kPa), thus having low potential for volatilization from soil or plant surfaces (Grover, 1984). Evidence to support this has been presented (Smith et al, 1986) in field trials where airborne residues were monitored using polyurethane foam plug air samplers measured at six heights (30, 50, 75, 100, 150, 200 cm) in the centre of a treated field. Air samplers at all six heights failed to trap measurable amounts of the herbicidal ester. It was concluded therefore, that post-application losses of diclofop-methyl by volatilization from the crop canopy or from the soil surface was minimal or nonexistent.

The complete absence of vapor flux of diclofop-methyl under the conditions of the above study can be attributed to low vapor pressure, hydrolysis, strong adsorption at the soil:air interface, and hydrolysis and rapid absorption at leaf surfaces (Grover, 1983). It was (Smith et al, 1986) demonstrated that a large portion (27% of applied ester) was intercepted by the crop canopy when a wheat field was sprayed. However, rapid absorption by the plants was observed with 50% loss of the ester in 4 h, decreasing opportunities for loss by volatilization.

3. Losses in Spring Run-off

A monitoring survey for several herbicides was conducted on the Ochre and Turtle Rivers, which flow into Dauphin Lake in western Manitoba (Muir et al, 1984), to determine the quantity of herbicidal contamination of this watershed by commercial use. Results of the survey indicated that transport of the widely used diclofop-methyl in this area to nontarget river systems was minimal. Diclofop-methyl was detected in the Turtle River at a concentration of 476 ng/L following a major high water event in late June but was undetected at other sampling times. The acid form was detected only, suggesting field run-off of the degradation product of this herbicide. Although run-off shortly after herbicide applications has been considered to be a major contributor to aquatic contamination, run-off due to storms in the prairies during the growing season are minimal. Major run-off occurs during spring snow melt in May and June (Muir et al, 1984). The study concluded that diclofop-methyl losses in a watershed is minimal from run-off. Point source contamination like spray drift and aerial deposition may be more significant contributors to prairie surface water contamination (Grover et al, 1985).

V. Toxicity of Diclofop-methyl

Several toxicological studies have been conducted over the past few years concerning the effect of diclofop-methyl and its metabolite on various biological species. Mammals, birds, fish and invertebrates have been utilized as test subjects to determine the toxicity of this widely used herbicide in both laboratory studies and simulated environmental contamination experiments. Most studies have concluded that under normal field use conditions, diclofop-methyl is of relatively low toxicity or is virtually nontoxic to the species examined. Under higher usage levels or accidental spills, however, the herbicide can present a significant toxicological problem to certain species.

1. Invertebrate

The importance of natural enemies of agricultural pests has led to the formation of a joint pesticide test program to determine the side effects of several common pesticides to beneficial arthropods. The Working Group "Pesticides and Beneficial Arthropods" was set up by the International Organization for Biological Control (IOBC) and the West Palaearctic Regional Section (WPRS) in 1974 (Franz et al, 1980, Hassan et al, 1983, Hassan, 1987). The extensive programme, which tested the toxicity of 62 pesticides on 19 beneficial organisms in 9 European countries from 1977 to 1985, used laboratory, semi-field and field tests. The toxicity of Illoxan was examined on several species in the laboratory under conditions of applied formulated material using the highest concentration registered for use, at 0.75% or 1.62 kg/ha. Toxicity was measured as any reduction in beneficial capacity (i.e. parasitism) or performance (i.e. laying) of the test arthropod, plus mortality as a result of exposure to the pesticide.

The first and second joint programs (Franz et al, 1980, Hassan et al, 1983) examined the side effect of Illoxan and other pesticide on six to thirteen different beneficial arthropods (entomophagous insects). Arthropod species were exposed with an initial contact to a fresh, dry pesticide film in cages with forced ventilation. The study concluded that Illoxan was harmless to slightly harmful to all natural enemies tested (Table 3). Because of its low toxicity to organisms tested, the duration of harmful activity (persistence) was not examined. Of the 40 pesticides tested, 14 of these, including Illoxan were recommended for use in integrated control programs because of their relatively low toxicity to the beneficial arthropods tested.

The third joint testing program (Hassan, 1987) further examined the effect of 22 pesticides on 18 beneficial organisms. Tests were designed to expose a relatively susceptible life stage of the organism and a more protected or robust life stage with directly sprayed pesticide. The results showed that Illoxan was relatively harmless to tested beneficial arthropods (Table 3) in both life stages. The study concluded that Illoxan was found to be less hazardous to relevant natural enemies of cereal, root and forage crops.

The toxic effect of diclofop-methyl on beneficial parasites was investigated (von Naton, 1983). The parasite, Phygadeuon trichops (Hymn Ichneumonidae) lives on various types of Delia. Several of these species, such as D. brassicae (cabbage fly), D. antiqua (onion fly), D. coarctata (wheat bulb fly) and D.florilega (bran fly) cause extensive damage to agricultural crops. Laboratory studies used the species Delia antiqua to determine the reduction in parasite numbers of Phygadeuon trichops in this host under spray conditions at the highest permissible concentration of Illoxan (0.75%). Results showed parasite reduction in the order of 28.5% and therefore was classified as slightly harmful to this agriculturally significant parasite.

2.Aquatic

The search for a simple, rapid method for the evaluation of a new pesticide led to the work by Walker (1984) to design a screening test for fate and toxicity of herbicides in the environment. A shake-flask screening test was developed which was used to evaluate the degradation rates and toxicity of the parent compound and its metabolites. Toxicity testing initially involved laboratory exposure of mysid shrimp (Mysidopsis bahia) and sheepshead minnow (Cyprinodon variegatus) to the test chemical. Preliminary screening of toxicity was conducted by determination of 96-hour minimum effective concentrations (MECs) prior to further toxicity testing. Testing of diclofop-methyl using these aquatic species in the preliminary screening tests gave results of 961 ug/L for Mysidopsis and 3000 ug/L for Cyprinodon, indicating very low toxicity to these species. Because of the high MEC values, further toxicity tests were not run concomitant with these screening evaluations.

Tank mixtures of pesticides are being increasingly used. To determine if mixtures may be more of a hazard to aquatic life than indicated by individual components, several commonly used mixtures were evaluated (Mattheissen et al, 1988). Rainbow trout fingerlings (Salmo gairdneri Richardson) were exposed to tank mixes in relative proportions approximating those recommended for application rates. A continuous flow test apparatus was used to evaluate 96 h LC_{50}s of both the individual components and the

mixtures to determine whether the effect was additive or synergistic.

Diclofop-methyl was evaluated using four mixtures commonly used in the UK. Joint toxicity was calculated by the reciprocal of x + y based on the 96 h LC_{50} of the mixture, and classed as additive, less than additive or synergistic. Results of the study were as follows:

Mixture	Measured Ratio of ai	LC_{50} of components (mg ai/l)	LC_{50} of mixture (mg ai/l)	1/(x + y)
Sportak Hoegrass	1:1.26	0.68 0.18	0.20	1.33
Calixin Hoegrass	1:1.33	0.30 0.09	0.16	0.81
Hoegrass Corbel	1:1.63	0.27 1.40	0.52	1.04
Radar Hoegrass	1:3.15	2.31 0.16	0.26	0.79

Only one of the mixtures tested, Sportak/Hoegrass, showed median lethal time versus toxic unit curves definitely to the left of the individual component curves, suggesting a possible synergistic effect. However, the apparent excess toxicity of 1.33 is relatively small. The study concluded that the results did not provide evidence that tank-mixing these pesticides would have a large unexpected effect on aquatic life.

3. Avian

A few studies have evaluated the effect of exposure of a number of avian species to Hoe Grass under both laboratory and field exposure conditions. Studies concerning the absolute toxicity of Hoe Grass to species tested suggested that this herbicide is of relatively low toxicity.

Studies of the inherent toxicity of diclofop-methyl were conducted on Japanese Quail (Cortunix japonica) (Hill et al, 1986, Westlake et al, 1988, Pesticide Science, 1981). Five-day subacute dietary toxicity tests on young (14-day old) Cortunix (Hill et al, 1986) were examined and compared for 193 potential environmental contaminants. The LC_{50}, defined as ppm active ingredient in a 5-day ad libitum diet calculated to kill 50% of the test population, was determined using fortified (technical grade chemical) grain feed in a preliminary range-finding test. Mortality, overt toxic signs, and food consumption were recorded

at 24 h intervals and compared to positive and negative controls. Compounds were classed into five groups based on the LC_{50} and of the total number of compounds tested, 63% were classified as "practically nontoxic" to Cortunix, with LC_{50}s of >5000 ppm. Hoelon was included in this class and no further detailed tests were conducted on it. No overt signs of toxicity or mortality were noted up to 5000 ppm over the 5-day feeding trial and total food consumption was essentially the same for both fortified grain and controls. This evidence for the nontoxic effects of diclofop-methyl to Cortunix was confirmed by a separate laboratory study (Westlake et al, 1988) which exposed Japanese quail at levels up to 1000 ppm for 2 weeks and at 20 ppm for up to 8 weeks and found no effect observed on tissue esterases, tissue derived plasma enzymes or relative liver weight. These parameters have been shown to be of value as indicators of the sub-lethal effects of pesticide exposure. Although hepatic cytochrome P_{450} significantly decreased at most treatment levels, the study concluded that based on lack of significant biochemical changes, there would not be any potential hazard to avian species from field application of diclofop-methyl.

The toxicity of Hoelon to avian species was further examined (Hoffman et al, 1984) using mallard eggs. The study involved the examination of the embryotoxicity of 42 environmental contaminants applied externally to mallard (Anas platyrhynchos) eggs in the laboratory. The LC_{50}s of commercial formulations of herbicides and insecticides in aqueous emulsion were measured by egg immersion. Fertile eggs were immersed on day 3 for 30 sec using concentrations of the active ingredient estimated as the amount expected after field spraying at a commonly used rate of 100 gal/A, and at half and five times the field level of application. Eggs were examined daily for mortality and embryos were removed on day 18. Any malformations or reduced growth in survivors at the end of the experiment were further examined histologically. Day three of development is a critical period for organogenesis in the mallard embryo and the first 8 to 9 days are generally critical, therefore this period was chosen for exposure. The results concluded that, in contrast to the study on Cotoxurn (Westlake et al, 1988), diclofop-methyl was classified as toxic (LC_{50}s of 7 to 40 lbs/A or less than 10 times field application rate). The LC_{50} of diclofop-methyl was determined to be 9.5 lb/A (at 100 gal/A) with a ratio of LC_{50}/field level of application of 6.3. The order of potential hazard based on absolute toxicity and in terms of the highest permissible field level of application was trifluralin > paraquat > prometon > diclofop-methyl > propanil > bromoxynil with MCPA > picloram > amitrole > 2,4,5-T > 2,4-D, glyphosate > atrazine, dicamba , dalapon. Further results in this study demonstrated reduced growth of embryos occurring at doses less than the LC_{50} and abnormal survivors at day 18 at doses equal or greater than LC_{50}, with malformations occurring in the eye.

4. Mammalian

Very few studies concerning the toxicity of Hoe Grass to mammals have been conducted to date. One study (Westlake et al, 1988) made use of wild trapped wood mice(Apodemus sylvaticus) and bank voles (Clethrionomys glareolus) to assess the hazards of chronic exposure of diclofop-methyl to wildlife. Laboratory experimentation exposed these species to wheat grain treated with technical grade diclofop-methyl at levels of 20, 200, 500 and 1000 ppm for 1 and 2 weeks and at 20 and 200 ppm for 4 weeks. The highest treatment level corresponds to approximately two and a half times the field application rate of 1.1 to 1.26 kg ai/ha. Toxicity was measured by biochemical (hepatic, plasma and brain enzymes) and histological changes by evaluation of liver and kidney samples.

Wood mice showed no significant effects at 20 ppm treatment; however, at 200 ppm, increases in relative liver weight, liver cytochrome P_{450} and plasma nitrophenyl acetate esterase (NPAE) occurred. In addition, increases in hepatocyte size (hypertrophy) and increased DNA content shown by increased hepatocyte binucleation and increased frequency of anuclear hepatocytes in lower concentrations occurred, leading to necrosis in higher treatment groups. At 500 and 1000 ppm, these changes occurred along with a severe increase in liver fatty degeneration, cuffing of blood vessels by leukocytes, increased hepatocyte size with single cell necrosis and loss of cytoplasmic protein. These histological findings are consistent with chronic hepatitis. Plasma GOT levels in these treated wood mice supported the histological liver findings as they were increased significantly in all treated mice. This indicated that considerable tissue damage and leakage from cells was occurring.

Trapped bank voles showed less significant biochemical changes at 200 and 1000 ppm exposure after 2 weeks. However, the relative liver weight increased significantly, liver NPAE activities decreased, plasma NPAE activity increased at the higher treatment and hepatic cytochrome P_{450} increased. The 200 ppm treatment resulted in greater histological changes in the vole livers compared to the mice livers. Inflammation was greater at 200 ppm than 1000 ppm, but regenerative replacement of necrotic hepatocytes, greater lipid degeneration and a decrease in cytoplasmic protein was observed at 1000 ppm.

Although the mainly hydropic enlargement leading to increased relative liver weights and diffuse hepatocyte necrosis represented significant toxicological effects on these wildlife species under laboratory exposure, these changes represent reversible, limited effects in mouse and vole livers. The study concluded that diclofop-methyl likely would not pose a hazard to

small mammals when applied at the maximum recommended field rate. The most significant effects to these wildlife species in the environment under conditions of exposure would be due to further pathological or physiological insult to the affected livers or environmental stress which could produce liver failure once the regenerative reserve capacity had been exceeded. Therefore, the inherent toxicity of diclofop-methyl to wood mice and voles is relatively low in the environment.

The effect of diclofop-methyl on mammalian enzyme systems has been further examined in a study which evaluated the effect on calmodulin-dependant cyclic nucleotide phosphodiesterase (PDE) in bovine brain tissue (Hertel et al, 1983). PDE has been identified in various tissues including brain, and also exists in plants as well as in fungi. It functions together with adenylate cyclase to regulate the cytoplasmic concentration of the second messenger cyclic AMP. Because PDE depends on the CA^{2+} activity in the cell, it is important in cooperation between the two second messengers, calcium ion and cyclic AMP. Hence, the regulation of a great variety of cellular processes depends on the activity of the calmodulin-dependant PDE. The study showed that diclofop-methyl stimulated the basal PDE activity approximately 2-fold at a concentration of 2×10^{-5} M and increased basal PDE activity 5-fold at 10^{-4} M. However, at the latter concentration, calmodulin-dependant PDE activity was decreased to about 50% of the control. The study suggested that sub-lethal toxicity of diclofop-methyl in mammals may be similar to the mode of action causing herbicidal activities in plants.

Acute toxicity of diclofop-methyl to rats and mice has been studied (Kolesnikov, 1984). The results indicated that diclofop-methyl is moderately toxic (class III type materials) with LD_{50}s in rats and mice of 870 and 586 mg/kg respectively, and with critical organs being the skin, respiratory organs and the eye. Clinical symptoms in mice and rats were alike. The intoxication signs developed gradually, reaching a maximum by the first day. Symptoms were decreased muscle tone, loss of movement and coordination, adynamia, and comatose condition, with death occurring in 2-3 days. Diclofop-methyl had moderate cumulative properties, was shown to give marked skin irritation and had skin resorption action.

The influence of such elementary factors as food on the intensity of metabolism of diclofop-methyl in accidental poisonings in man was investigated using male rats fed various levels of vitamins, protein and fat under exposure to the herbicide (Kolesnikov, 1985). The protective action of food components to activate specific enzymes and stabilize membranes was examined by injecting white male rats with 87 mg/kg into the stomach daily during the last ten days of the feeding period. The dosage was chosen based on the LD_{50} of rats of 110 mg/kg, as

well as the dosage and length of exposure expected from occupational exposure to man. Low and high protein and fat diets were fed to the animals over 30 d, and liver levels of aminopyrine demethylase, aniline hydroxylase and liver cytochrome P_{450} (by electron paramagnetic resonance) as well as plasma aspartate and alanine aminotransferase were monitored throughout the study. Results indicated that rats fed a diet of low fat did not show significant effects on enzyme activity or induction under daily administration of diclofop-methyl. However, high dietary lipid and protein showed significant increases in activity of enzymes measured. High dietary protein increased activity of aminopyrinemethylase by 46%. High dietary fat gave increases of aminopyrinemethylase to 128%. High fat and protein gave increases in cytochrome P_{450} by 33% and 54% respectively and in addition, decreased toxicity and even the prevention of toxic action was noted. The most significant effect was demonstrated in the test group consuming low protein diets where both low activity of enzymes and relative increases in intoxication by diclofop-methyl was noticed. It is well established that protein is necessary for the proper metabolism of xenobiotics. Induction of liver microsomal monooxygenase system is decreased in protein malnutrition, decreasing metabolism. Weight of survived and poisoned rats of the low protein diet group was much lower than the control group weight with a ratio of <0.05. Appetite of rats in fat or protein deficits during diclofop-methyl injection was decreased as well. The study concluded that in occupational exposure and accidental poisonings, adequate dietary levels of protein and fat could be significant in the prevention of toxic effects and act as an antidote in potential poisonings by the herbicide diclofop-methyl.

5. Bacteria

There was no significant decrease in the rate of nitrate and nitrite reduction noted in shaken flask systems containing sand and sandy loam and treated with either technical diclofop-methyl or Hoe-Grass (Kuchnicki, 1987).

VI. Summary

Diclofop-methyl is a selective herbicide which has been studied in aquatic and terrestrial systems. It is relatively nonpersistent under normal field usage and degradation is nearly complete by the end of the growing season. Research has indicated that carry-over of residues to the next growing season is negligible and poses no problem to crops the following year.

Contamination of aquatic systems does not appear to be extensive in heavily sprayed areas except during high run-off events in spring. Studies have suggested that degradation in

water is rapid and complete in days to weeks, dependent on conditions of the system. Therefore, although some contamination of water systems may occur through natural processes in heavily sprayed areas, the herbicide does not persist in the system to any great extent. Further research on the degradation and effects of aquatic pollution by diclofop-methyl is needed.

The degradation of diclofop-methyl has been studied extensively in soils. Findings show a rapid hydrolysis of the ester to its corresponding acid, which also has herbicidal activity. Subsequent degradation of the acid is much slower, with formation of the phenol and phenetole forms, as well as other nonidentified metabolites from the acid. Degradation progresses further with the mineralization of aromatic rings, liberating CO_2. Binding of unidentified degradation products has been shown to occur, however, these bound residues appear to be neither persistent nor phytotoxic by the end of a growing season. Further characterization of the nature and significance of these residues is required.

The rate of loss of diclofop-methyl is dependent on a number of factors. The extent of microbial activity significantly affects the rate of acid loss. Persistence on soil under anaerobic conditions greatly increases, due to loss of microbial degradation. Soil moisture and pH influence the hydrolysis of the ester and the persistence of the applied herbicide. In addition, the characteristics of the soil, such as its texture, organic matter, and clay, silt and sand components will affect persistence of diclofop-methyl by influencing hydrolysis and degradation rates, as well as adsorption to soil fractions. Optimum conditions for degradation appear to be in moist soils at a neutral to basic pH in fine-textured soil types with high clay content.

Loss of field-applied diclofop-methyl to nontarget systems by natural routes is limited. Transport by leaching through soil and release into the atmosphere by volatilization is negligible.

The effects of diclofop-methyl on biological species investigated is generally classified as nontoxic or of low toxicity. Invertebrates and avian species are relatively resistant to harmful effects caused by this herbicide. However, teratogenic affects have been observed under chronic exposure of mallard eggs. Acute toxicity to mammalian species is low to moderate. Diclofop-methyl has been classified as moderately toxic (class III compound) based on rodent studies. Chronic toxicity to mice and voles was limited, causing reversible enzyme and histological sub-lethal effects. From the limited data available, it is evident that diclofop-methyl, based on its low toxicity to wildlife studied coupled with its low persistence and minimal potential for transport to nontarget systems, does not

pose a hazard to wildlife under its present registered use. However, acute toxicity may be a problem to wildlife and man under accidental spill events, and no information is available on potential hazards to man with low level occupational exposure.

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Table 1. Characteristics of Diclofop-methyl

chemical name:	2-[-4-(2,4-dichlorophenoxy)phenoxy] methyl-propanoate
common names:	HOE-23408 Hoelon (U.S.) Hoe-Grass (CAN) Illoxan
molecular formula	$C_{16}H_{14}C_{12}O_4$
molecular weight:	341
Specific gravity:	1.3 gm/cm^3 at 40 C
Melting point:	39-41 C
Boiling point:	175-176 C at 0.1 mm/Hg
UV irradiation:	decomposes readily
Vapor pressure:	0.258 x 10^{-6} mm/Hg at 20 C

Solubility (at 20 C):

solvent	g/100 ml
water	0.3
acetone	249.0
xylene	253.0
ethanol	11.0

Table 2. Soil characteristics summary of fate studies

Source	Soil type	pH	Sand%	Silt%	Clay%	OM%	FC%
Gaynor, 1984	Fox sandy loam	7.5					1.0
		6.5					1.0
		5.5					0.9
	Brookston clay	7.5					3.6
Martens, 1977	loamy sand	6.6	79.4	12.1	8.5	3.20	
	sandy loam	5.2	62.4	32.6	5.0	0.95	
Mulder et al, 1979	Fordville loamy sand	7.1	86.5	6.0	7.5	2.6	11
	Tiffany sandy loam	7.8	74.0	13.2	12.8	4.6	21
	Fargo sandy loam	7.8	71.0	12.3	16.7	3.7	23
	Northfield loam	6.4	52.0	30.0	18.0	2.5	14
	Fargo clay	7.1	19.0	32.0	49.0	6.4	38
Smith, 1977, 1979	Jameson sandy loam	7.5	85	9	6	3.2	11
	Melfort silty clay	5.2	32	38	30	11.7	36
	Regina heavy clay	7.7	5	26	69	4.2	40
Smith et al, 1986		7.7	1	27	70	3.0	
Wink et al, 1987	sand	5.2	89	8	3	1.8	21
	sandy loam	6.3	69	26	5	5.1	44
Wu et al, 1976	Teller sandy loam	5.7	57	23	20	1.3	
	Cobb sand soil	7.3	93	4	3	0.6	

Table 3.

Results of the IOBC/WPRS-Working Group
"Pesticides and Beneficial Organisms"

Toxicity of the Herbicide Illoxan

Species	Result
Initial Toxicity	
Trichogramma	2
Pales	1
Phygadeuon	1
Leptomastix	2
Coccygomimus	1
Chrysopa	1
Encarsia	1
Syrphus	2
Egg parasites of Lepidoptera	
Trichogramma - susceptible stage	2
- robust stage	1

1 = harmless (<50%)
2 = slightly harmful (50-79%)

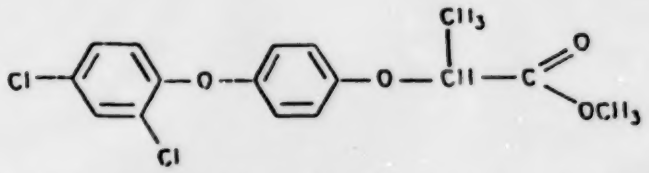
Table 4. Summary of Analytical Methods for Diclofop-methyl

Sample	Method	Source
Soil	EC/GC, ester and acid polar solvent extraction	Jacobson, 1984 Johnstone, 1985 Novitskaia, 1984 Smith, 1976, 1977, 1979a, 1979b Smith et al, 1986
	TLC, SC, radiolabelled herbicide	Gaynor, 1984 Martens, 1978 Smith, 1977, 1979a,b
	evaluation of enantiomers with HPLC	Wink, 1988
	soil bound residue extraction -combustion	Gaynor, 1984 Smith, 1977
	-NaOH, hot triethanolamine extractions	Smith, 1979a,b
	CO_2 mineralization trapping	Martens, 1978
	leaching studies-thick layer chromatography	Mulder et al, 1979
	bioassay methods for persistence	Mulder et al, 1979 Wu et al, 1976
Water Samples	EC/GC and MS/GC polar solvent extraction	Knauf et al, 1977 Lee et al, 1983 Muir et al, 1984 Walker, 1984
	Sediments analysis-GC - shake flask screening	Knauf et al, 1977 Lee et al, 1983 Walker, 1984
Plant Samples	EC/GC and MS/GC polar solvent extraction	Novitskaia, 1984 Smith, 1977 Smith et al, 1986 Specht et al, 1981
	TLC, SC, radioautography, radiolabelled herbicide	Jacobson et al, 1984 Shimabukuro et al, 1979

Table 4. cont'd

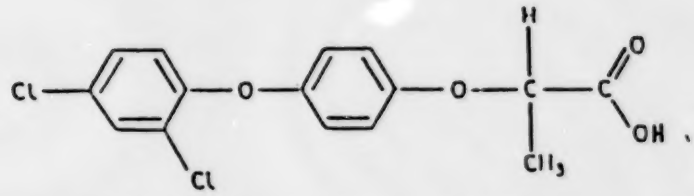
Sample	Methods	Source
Plant Samples	HPLC	Shimabukuro et al, 1979
Biological	mouse bodies and kidneys	Pesticide Science, 1981
Other	enzyme immunoassay and fluoroimmunoassay	Schwalbe et al, 1984

Figure 1. Diclofop-methyl (from Schwalbe, M., 1984)



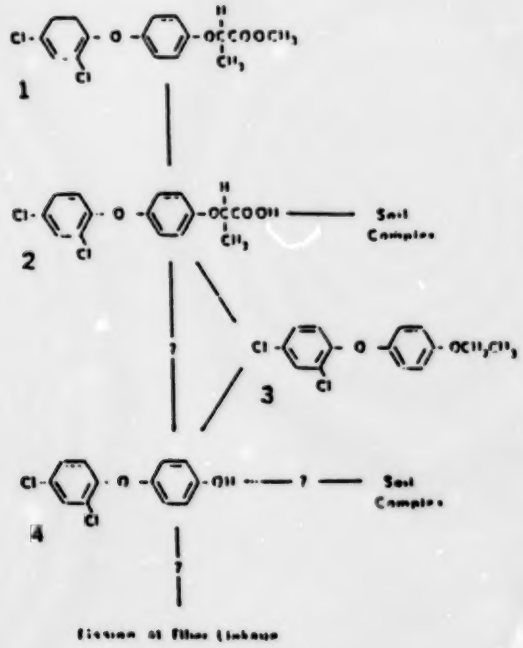
methyl 2-[4-(2,4-dichlorophenoxy)phenoxy]propionate

Figure 2. Diclofop (from Martens, R., 1978)



(RS)(±)-2-[4-(2,4-Dichlorophenoxy)phenoxy]propionic acid

Figure 3. Suggested pathway for degradation in soil (from Smith, A., 1977)



1. diclofop-methyl
2. diclofop acid
3. dichlorophenoxyphenetole